

FORM PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 268/249	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/088940	
INTERNATIONAL APPLICATION NO. PCT/EP00/08970		INTERNATIONAL FILING DATE September 14, 2000		PRIORITY DATE CLAIMED September 23, 1999	
TITLE OF INVENTION ALKYLDIPROPYLENETRIAMINES AND THEIR ADDUCTS AS HARDENERS FOR EPOXY RESINS					
APPLICANT(S) FOR DO/EO/US Wofgang SCHERZER; Jörg VOLLE					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau) b. <input checked="" type="checkbox"/> has been communicated by the International Bureau c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). a. <input type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4) 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11 to 20 below concern document(s) or information included: 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input checked="" type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information: PCT/IB/308					

10/088940
JC13 Rec'd PCT/PTO 21 MAR 2002

CERTIFICATE OF MAILING
(37 C.F.R. §1.10)

I hereby certify that this paper (along with any referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as 'Express Mail Post Office To Addressee' in an envelope addressed to Box PCT, Commissioner for Patents, Washington, D.C. 20231.

EV 056390681 US

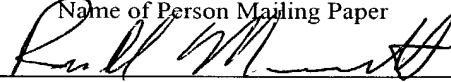
Express Mail Label No.

March 23, 2002

Date of Deposit

Russell Morrisette

Name of Person Mailing Paper



Signature of Person Mailing Paper

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: U.S. National Stage Application of PCT/EP00/08970)	Group Art Unit: to be assigned
)	
Inventor: Scherzer, W. et al.)	Examiner: to be assigned
)	
Serial No.: to be assigned)	
)	
Filed: March 21, 2002)	
)	
For: ALKYLDIPROPYLENETRIAMINES AND THEIR ADDUCTS AS HARDENERS FOR EPOXY RESINS)	
)	

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

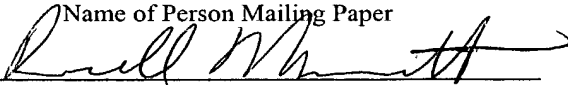
Prior to examination on the merits, please enter the following amendments to the pending claims of the above-cited application.

Please substituted the following amended claims 1 to 7 for the pending claims of the same number. Please enter new claim 8.

CERTIFICATE OF MAILING
(37 C.F.R. §1.10)

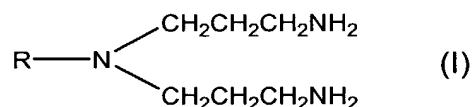
I hereby certify that this paper (along with any referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as 'Express Mail Post Office To Addressee' in an envelope addressed to the Commissioner for Patents, Washington, D.C. 20231.

EV056390681US
Express Mail Label No.
March 21, 2002
Date of Deposit

Russell Morrisette
Name of Person Mailing Paper

Signature of Person Mailing Paper

CLEAN COPY OF AMENDED CLAIMS

1. (Amended) A curable composition comprising
 - a) an epoxy resin having on average more than one epoxide group per molecule and at least one member selected from the group consisting of
 - b1) an alkyldipropylenetriamine of the general formula (I) and
 - b2) an adduct of an alkyldipropylenetriamine of the general formula (I) with an epoxide compound having on average at least one epoxide group per molecule,



in which R is a hydrocarbon radical having 8 to 22 carbon atoms.

2. (Amended) A curable composition according to claim 1, further comprising one or more members selected from the group consisting of diluents, other amine components and customary auxiliaries and additives.
3. (Amended) A curable composition according to claim 1, wherein the composition is derived from compounds of the formula (I) with different hydrocarbon radicals R.
4. (Amended) A curable composition according to claim 1, wherein component a) is a bisphenol A diglycidyl ether or bisphenol F diglycidyl ether.

- WP-19528.1

Patent
Attorney Docket: 268/249

REMARKS

Claims 1-7 are present in the above-referenced International Application, upon which this National Stage Application is based. New claim 8 encompasses the material canceled by the amendment to claim 1. Accordingly, no new matter has been added.

In view of the foregoing amendments, it is believed that the instant claims are now in better condition for examination on the merits. Early favorable action is therefore respectfully solicited.

No fee is believed necessary for the filing of this submission. However, should any fee be deemed required for entry, the Commissioner is authorized and requested to charge any amounts due on account of the present submission to the Deposit Account of the undersigned attorneys, which is:

Deposit Account No. 12-2475.

Respectfully submitted,

LYON & LYON LLP

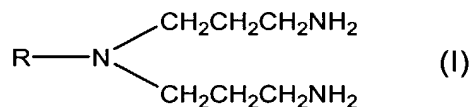
Dated: March 21, 2002

By: Charles M. Doyle
Charles M. Doyle
Reg. No. 39,175

633 West Fifth Street, Suite 4700
Los Angeles, California 90071-2066
(914) 681-8851

VERSION WITH MARKINGS TO SHOW CHANGES MADE

1. (Amended) A curable composition comprising
 - b) an epoxy resin having on average more than one epoxide group per molecule and at least one member selected from the group consisting of
 - b1) an alkyldipropylenetriamine of the general formula (I) [and/or] and
 - b2) an adduct of an alkyldipropylenetriamine of the general formula (I) with [b3)] an epoxide compound having on average at least one epoxide group per molecule,



in which R is a hydrocarbon radical having 8 to 22 [, preferably 10 to 20,] carbon atoms.

2. (Amended) A curable composition according to claim 1, further comprising one or more members selected from the group consisting of diluents, other amine components and customary auxiliaries and additives [c) diluents and/or other amine components and/or other customary auxiliaries and additives].
3. (Amended) A curable composition according to claim 1 [either claim 1 or claim 2], wherein the composition is derived from compounds of the formula (I) with different hydrocarbon radicals R.

4. (Amended) A curable composition according to claim 1 [any one of claims 1 to 3], wherein component a) is a bisphenol A diglycidyl ether or bisphenol F diglycidyl ether.
5. (Amended) A curable composition according to claim 1 [any one of claims 1 to 4], wherein component b) is a bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, cresyl glycidyl ether or fatty alcohol glycidyl ether.
6. (Amended) A cured composition comprising a composition according to claim 1 [any one of claims 1 to 5].
7. (Amended) The use of a composition according to claim 1 [any one of claims 1 to 5] for coating mineral and metallic substrates.

Claim 8 is new.

Alkyldipropylenetriamines and their adducts as hardeners for epoxy resins

The present invention relates to alkyldipropylenetriamines and their adducts with epoxide compounds having on average at least one epoxide group per molecule as hardeners for epoxy resins and to the use of curable compositions based on these alkyldipropylenetriamines and adducts and epoxy resins for coating mineral and metallic substrates.

Curable compositions based on amine curing agents and epoxy resins are widely used in industry to coat and enhance metallic and mineral substrates. Amine curing agents used in particular are aliphatic, cycloaliphatic or aromatic amines and also polyaminoamides with or without imidazoline groups.

The mechanical and physical properties of the curable compositions based on these amines are adequate for numerous applications.

Especially for the coatings sector, however, there is a requirement for binder systems which are surface tolerant, i.e., which exhibit good adhesion even on substrates that are difficult to coat, such as moist substrates or unpretreated metal panels, for example, and which ensure the very best protection of the substrate, e.g. corrosion protection. There is also a requirement for rapid initial curing of the binder systems following application to the substrates, even at low temperatures, in order, for example, to ensure that the substrates can soon withstand loading or be coated further.

High early water resistance of the still uncured film (for example, by forming droplets at high relative atmospheric humidities) is an important criterion, as is a low viscosity of the binder, so that it can still be processed even at low temperatures.

Known hardeners for epoxy resins which afford relatively good corrosion protection and exhibit serviceable adhesion even on difficult substrates include polyaminoamides, which normally contain imidazoline groups. These compounds are prepared by condensing generally unsaturated, long-chain fatty acids with polyethylenepolyamines. The disadvantage of these compounds is their high viscosity at low temperatures ($< 15^{\circ}\text{C}$) and also the slow

rate of initial cure and/or through-cure. Moreover, compounds of this type possess relatively high colour numbers.

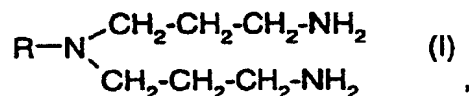
It was therefore an object of the present invention to eliminate these disadvantages.

This object is achieved through the use of the curable compositions of the invention, comprising alkyldipropylenetriamines and/or their adducts with epoxide compounds which contain on average at least one epoxide group per molecule with epoxy resins.

It has surprisingly been found that the alkyldipropylenetriamines and/or their adducts of the invention, although similar in structure to the polyaminoamides with or without imidazoline groups, possess a much higher rate of initial cure and/or through-cure, especially at low temperatures of $< 15^{\circ}\text{C}$. Moreover, these compounds have, in comparison, a much lower viscosity and colour number.

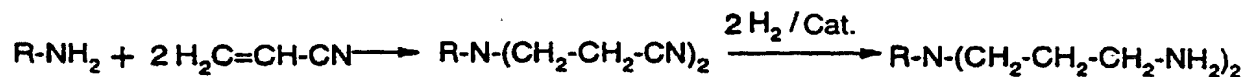
The invention provides curable compositions comprising

- a) an epoxy resin having on average more than one epoxide group per molecule and
- b1) an alkyldipropylenetriamine of the general formula (I) and/or
- b2) an adduct of an alkyldipropylenetriamine of the general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule



in which R is a hydrocarbon radical having 8 to 22, preferably 10 to 20, carbon atoms.

The compounds of the formula (I) are normally prepared by cyanoethylation of amines (fatty amines) and subsequent hydrogenation in accordance with conventional methods. The amines or, respectively, fatty amines are reacted with acrylonitrile, and then the cyanide groups are hydrogenated in the presence of a catalyst. Schematically, the reaction sequence is as follows:



The fatty amines used preferably as reactants for the cyanoethylation are mixtures of long-chain primary alkylamines, obtained from mixed glycerol esters of medium and higher fatty acids with an even number of carbons, as occur in plant or animal bodies. For example,

bovine tallow contains almost 100% (esterified) fatty acids having a carbon chain length of 14, 16 and 18 carbon atoms. The bovine tallow fatty amines obtained from bovine tallow are available commercially as tallow fatty amine, for example as Genamin® TA100 (Clariant). Therefore, if adducts of the invention are prepared starting from fatty amines of natural products, the products of the general formula (I) comprise mixtures of compounds with different chain lengths R. The chains R have approximately 8 to 20 carbon atoms, not more than approximately 22 carbon atoms, and may either be saturated or contain multiple bonds and may be either straight-chain or branched. Further examples of commercially available fatty amines which may be used in accordance with the invention, besides tallow fatty amine, are saturated straight-chain fatty amines such as dodecylamine, tetradecylamine, for example, saturated, branched fatty amines such as isotridecylamine, for example, unsaturated and saturated fatty amines and fatty amine mixtures, such as coconut fatty amine, oleylamine, rapeseed oil fatty amine, for example, or else stearylamine.

The present invention provides b2) adducts of compounds of the formula (I) with epoxide compounds containing on average at least one epoxide group per mole (b3). The adducts of the invention are prepared by known methods, by adding the epoxide compounds dropwise at 50°C - 100°C with stirring to the initial charge of alkyldipropylenetriamine and then stirring the mixture at the same temperature for about 30 minutes until formation of adducts is at an end.

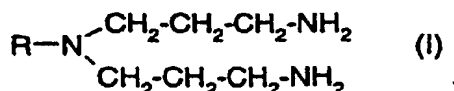
Also used are what are known as "isolated adducts", which are prepared with an excess of alkyldipropylenetriamine. In this case, from 1.5 to 10, preferably 4-6, times the molar amount of amine are introduced as the initial charge and the epoxide compound is added dropwise with stirring, judiciously at 50-100°C. Subsequently, the excess amine is removed by distillation under reduced pressure.

The invention further provides a process for preparing the adduct, which comprises heating an alkyldipropylenetriamine of the formula (I) to reaction temperature (50-100°C), subsequently adding at least one epoxide compound (F) having on average at least one epoxide group in the molecule, with continued stirring, and finally, after the formation of adducts has ended, removing any excess alkyldipropylenetriamine from the reaction mixture.

In accordance with the invention, both the compounds of the formula (I) and the adducts with epoxide compounds that have derived from the compounds of the general formula (I) may be used as hardeners for epoxide compounds. Similarly, mixtures comprising at least one compound of the formula I and at least one adduct of compounds of the formula I with epoxide compounds may be used as hardeners for epoxide compounds. Similarly, mixtures of compounds of the formula (I) or, respectively, their adducts may be used in which the compounds of the formula (I) may have hydrocarbon radicals R which are different in terms of the respective chain length (8 to 20 carbon atoms), degree of branching and bond order. Moreover, the curable compositions of the invention may comprise further amine curing agents, with or without the use of solvents, plasticizers, UV stabilizers, dyes, pigments and fillers.

The invention therefore additionally provides curable compositions comprising

- a) an epoxy resin having on average more than one epoxide group per molecule and
- b1) an alkyldipropylenetriamine of the general formula (I) and/or
- b2) an adduct of an alkyldipropylenetriamine of the general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule



in which R is a hydrocarbon radical having 8 to 22, preferably 10 to 20, carbon atoms, and, if desired, further optional components selected from

- c) diluents, other amine components and other customary auxiliaries and additives.

The modifiers c) may be added equally to the hardener b) of the invention, to the resin a), with the exception of the amine component, or to the curable composition.

The curable compositions of the invention, comprising compounds of the general formula (I) and their adducts, are preferably adjusted with the modifiers to a preferred mixing ratio of 50-100 parts by weight of hardener per 100 g of epoxy resin (a). Depending on the establishment of desired end properties, the mixing ratios may also be below 50 and, respectively, above 100 parts by weight of hardener per 100 g of resin (a).

The fraction of diluents should not exceed 40%, based on the hardener, since otherwise there is too great a drop in the mechanical data.

The ratio of reactive groups of the compounds of the general formula (I) and their adducts and any additional amines to the epoxide groups (a) and, if present, the epoxide compounds as per (b3) is preferably established at equivalence. Here too, however, depending on the establishment of desired properties, there may be deviations, in some cases very sharp, from equivalence, including both upward and downward deviations. The fraction of the hardeners of formula I and/or their adducts in the curing agent is between 10 and 70%, preferably between 20 and 50%.

As diluents it is possible to use both compounds which largely remain in the thermoset after curing, such as high-boiling alcohols and ethers such as benzyl alcohol, ethylene glycol, propylene glycol, butyl diglycol, etc., and compounds which predominantly evaporate from the coating in the course of curing, such as xylene, butanol, methoxypropanol, and also water, for example.

As additional amine components and for establishing the end properties it is possible to use all customary amines, such as polyethylene polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, etc.;

polypropylenepolyamines such as dipropylenetriamine, tripropylenetetramine, and also the polyamines obtained by cyanoethylation of polyamines, especially of ethylenediamine, and subsequent complete or partial hydrogenation;

aliphatic amines such as diaminoethane, diaminopropane, neopentanediamine, diaminobutane, hexamethylenediamine, 2,2,4(2,4,4)-trimethyl-1,6-hexamethylenediamine; cycloaliphatic polyamines such as isophoronediamine, diaminocyclohexane, norbornanediamine, 3(4),8(9)-bis(aminomethyl)tricyclo[5.2.1.0]decane (TCD-diamine), 1,3-bis(aminomethyl)cyclohexane, bis(aminomethylcyclohexyl)methane; heterocyclic polyamines such as N-aminoethylpiperazine, 1,4-bis(aminopropyl)piperazine; aliphatic amines such as xylylenediamine; polyoxyalkylenepolyamines; aromatic amines, such as diaminodiphenylmethane, for example; polyaminoamides with or without imidazoline groups, such as condensation products of monomeric or dimeric fatty acids with polyethylenepolyamines, for example.

The epoxide compounds (b3) used for forming adducts with the aforementioned alkyldipropylenetriamines are the known and commercially customary products having at least one epoxide group per molecule. Preference is given in accordance with the invention

to glycidyl ethers based on monohydric or polyhydric phenols, such as phenol, cresol, bisphenol A, bisphenol F, novolaks, monohydric or polyhydric aliphatic alcohols having 4 to 18 carbon atoms, such as butanol, butanediol, hexanol, hexanediol, fatty alcohols having a chain length of 8 to 18 carbon atoms, polyoxyalkylene glycols such as diethylene glycol, dipropylene glycol, polyoxypropylene glycol, polyoxyethylene glycols, diethylene glycol monobutyl ether, and also epoxide compounds prepared by direct epoxidation, such as styrene oxide. As epoxide compound (b3) preference is given in particular to bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, cresyl glycidyl ether and fatty alcohol glycidyl ethers.

The degree of adduct formation may be varied within wide limits and is influenced by the nature of the amine compound and by the nature of the epoxide compound, and may also be tailored to the respective field in which the curable composition is employed.

Positive results are generally always obtained using from 0.1 to 1 mol of the epoxide compound per mole of the amine compound, so that on average there are more than 2 free amine hydrogens in the adduct.

The epoxide compounds (a) used in accordance with the invention are commercially customary products having on average more than one epoxide group per molecule, and are derived from monohydric and/or polyhydric and/or polycyclic phenols, especially bisphenols, and also novolaks, for example, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether. An extensive listing of these epoxide compounds may be found in the handbook "Epoxidverbindungen und Epoxidharze" [Epoxide Compounds and Epoxy Resins] by A.M. Paquin, Springer Verlag, Berlin, 1958, Chapter IV, and in Lee & Neville, "Handbook of Epoxy Resins", 1967, Chapter 2. It is also possible to use mixtures of two or more epoxide compounds (a). Preference is given in accordance with the invention to mixtures of glycidyl ethers based on bisphenol A, bisphenol F or novolaks with what are known as reactive diluents, such as monoglycidyl ethers of phenols or glycidyl ethers based on monohydric or polyhydric aliphatic or cycloaliphatic alcohols, for example. Examples of such reactive diluents are phenyl glycidyl ether, cresyl glycidyl ether, p-tert-butylphenyl glycidyl ether, butyl glycidyl ether, C12-C14 alcohol glycidyl ethers, butane diglycidyl ethers, hexane diglycidyl ethers, cyclohexanedimethyl diglycidyl ethers or glycidyl ethers based on polyethylene glycols or polypropylene glycols. If necessary, the viscosity of the epoxy resins may be

TABLE 1. *Continued*

The invention therefore further provides, in addition, the cured compositions of the invention.

Analytical methods

Viscosity

Measured with a Haake RV 20 rotational viscometer in accordance with the manufacturer's instructions.

Colour number

Measured in accordance with DIN 53 995 using the Lovibond colorimeter (Gardner colour number, APHA colour number).

Amine number

Measured in accordance with DIN 16 945.

Tecam value

Value for the gel time measured with the Tecam gelation timer GT3 from Techne, Cambridge, GB, at 23°C and 50% relative atmospheric humidity.
Sample mixture of resin and hardener and accelerator = 250 g.

Shore D hardness

Measured with the instrument type 38009 from Karl Frank GmbH on test specimens of 30 mm in diameter and 6 mm in thickness after 1 day and 7 days and after 2 days and 24 hours of storage at 70°C.

Early water resistance/blushing of the film on water exposure

Sample preparation:

The calculated amounts of epoxy resin and amine hardener are weighed out into the mixing vessel and mixed thoroughly for approximately 2 minutes using a spatula without incorporating air to an excessive extent. Local inhomogeneities show up as smearing and are to be avoided.

A 500 µm film-drawing frame from Erichsen is placed on a glass plate which has been cleaned with acetone and then dried, and the frame is filled with approximately 15 g of the reactive mixture and drawn uniformly over the free area. The freshly coated glass plates are

immediately placed in the corresponding controlled-climate chambers, typically at a relative atmospheric humidity (RH) at 23°C of approximately 95%, at 10°C of approximately 80%.

To determine the early water resistance, the glass plates are brought back into the testing laboratory after 24 h of curing.

For the test, evaluation figures (along the lines of DIN 53230) are awarded:

0 = no defect

up to 5 = very severe defects.

In the case of precision differentiation, using comparison samples, for example, gradations of 0.5 are possible.

Approximately 0.5 ml of fully deionized water is applied by pipette to an area of each plate, and is dabbed off with cellulose after 60 minutes.

An assessment is made of the extent of coloration/blushing of the film at the water-exposed area.

Examples

Example 1 (Hardener)

N,N-Bis-amino-propyl-tallow fatty amine, prepared by reacting tallow fatty amine (a mixture of saturated and unsaturated alkylamines having 14-20 carbon atoms) with acrylonitrile and then hydrogenating the cyanide groups.

Example 2 (Hardener + diluent)

90 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and 10 g of benzyl alcohol are homogenized at room temperature.

Example 3 (Adduct + diluent)

80 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and 10 g of benzyl alcohol are introduced into a reaction vessel, then 10 g of a bisphenol A diglycidyl ether having an epoxide equivalent weight of 185 are added continuously over the course of approximately 20 minutes at 60-90°C.

Stirring is continued for about 10 minutes and then the mixture is cooled to room temperature.

Example 4 (Adduct + diluent)

The following are reacted in accordance with Example 3:

80 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and
10 g of cresyl glycidyl ether (epoxide equivalent approximately 180), and also
10 g of benzyl alcohol.

Example 5 (Adduct + diluent)

The following are reacted in accordance with Example 3:

90 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and
10 g of a long-chain aliphatic glycidyl ether having an epoxide equivalent weight of 315, and
10 g of benzyl alcohol.

Example 6 (Hardener + amine co-hardener + diluent)

40 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1,
27 g of isophoronediamine and
33 g of benzyl alcohol
are homogenized at room temperature.

Example 7 (Adduct + diluent)

The following are reacted in accordance with Example 3:

50 g of lauryldipropylenetriamine (prepared as per Example 1 on the basis of laurylamine
(alkylamine mixture having 8-18 carbon atoms per molecule)) and
20 g of a commercially customary glycidyl ether based on bisphenol A, having an epoxide
equivalent weight of 185 g/eq, and
30 g of benzyl alcohol
are homogenized at room temperature.

Example 8 (Comparative hardener)

Standard commercial polyaminoimidazoline, prepared by condensing triethylenetetramine
and tall oil fatty acid by conventional techniques.

Example 9 (Comparative adduct + diluent)

80 g of the polyaminoimidazoline as per Example 8 and 10 g of benzyl alcohol are introduced into a reaction vessel, then 10 g of a bisphenol A diglycidyl ether having an equivalent weight of 185 are added continuously over the course of approximately 20 minutes at 60-90°C.

The mixture obtained is subsequently stirred for 10 minutes and then cooled to room temperature.

Example 10 (Comparative hardener)

Standard commercial polyaminoimidazoline, prepared by condensing triethylenetetramine and dimerized talloil fatty acid by a conventional technique.

The properties and measurements obtained for Examples 1-10 are listed in Table 1.

Table 1

Example/ Measurements	1	2	3	4	5	6	7	8	9	10
Viscosity in mPa.s/25°C	26	33	141	40	35	24	195	250	1720	16000
Amine number mg KOH/g	430	385	345	385	385	350	275	390	312	390
Colour number (Gardner)	<1	1	1-2	1-2	1	<1	<1	8	7	8
g hardener per 100 g resin ¹	50	55	60	60	60	50	100	50	60	50
Tecam value (min)	175	103	102	135	168	76	85	180	205	120

Shore D hardness development at 10°C:

1 Day	21	28	11	10	5	43	54	0	0	11
2 Days	52	63	49	45	37	68	72	37	20	49
Final hardness ²	77	76	78	76	74	80	80	78	77	75

Early water resistance after 24-hour storage at:

10°C/80% RH	0.5	0	0	0	1	2	1-2	3	4	3
23°C/50% RH	0	0	0	0	0	0	0	1	3	2

Notes:

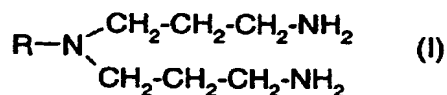
RH = relative atmospheric humidity

¹⁾ Araldite GY 250 = commercial epoxy resin based on bisphenol A, epoxide equivalent weight: 185

²⁾ Curing for 2 days at room temperature and 24 hours at 70°C

WHAT IS CLAIMED IS:

1. A curable composition comprising
 - a) an epoxy resin having on average more than one epoxide group per molecule and
 - b1) an alkyldipropylenetriamine of the general formula (I) and/or
 - b2) an adduct of an alkyldipropylenetriamine of the general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule



in which R is a hydrocarbon radical having 8 to 22, preferably 10 to 20, carbon atoms.

2. A curable composition according to claim 1, further comprising c) diluents and/or other amine components and/or other customary auxiliaries and additives.
3. A curable composition according to either claim 1 or claim 2, wherein the composition is derived from compounds of the formula (I) with different hydrocarbon radicals R.
4. A curable composition according to any one of claims 1 to 3, wherein component a) is a bisphenol A diglycidyl ether or bisphenol F diglycidyl ether.
5. A curable composition according to any one of claims 1 to 4, wherein component b) is a bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, cresyl glycidyl ether or fatty alcohol glycidyl ether.
6. A cured composition comprising a composition according to any one of claims 1 to 5.
7. The use of a composition according to any one of claims 1 to 5 for coating mineral and metallic substrates.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21679 A1

(51) International Patent Classification⁷: C08G 59/50,
59/18

Wolfgang [DE/DE]; Schenkstrasse 10, 59192 Bergkamen
(DE). VOLLE, Jörg [DE/DE]; Luisenstrasse 37a, 59379
Selm/Bork (DE).

(21) International Application Number: PCT/EP00/08970

(22) International Filing Date:
14 September 2000 (14.09.2000)

(74) Agent: HOECHST, Bruno, Werner; Vantico AG,
Patents/Scientific Information, Klybeckstrasse 200,
CH-4057 Basel (CH).

(25) Filing Language: English

(81) Designated States (*national*): AU, BR, CA, CN, HU, JP,
KR, MX, PL, RU, TR, US.

(26) Publication Language: English

(30) Priority Data:
199 45 643.7 23 September 1999 (23.09.1999) DE

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE).

(71) Applicant (*for all designated States except US*): VAN-
TICO GMBH & CO. KG [DE/DE]; Ernst-Scher-
ing-Strasse 14, 59192 Bergkamen (DE).

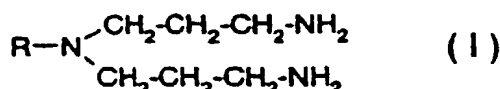
Published:
— With international search report.

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): SCHERZER,

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: ALKYLDIPROPYLENENTRIAMINES AND THEIR ADDUCTS AS HARDENERS FOR EPOXY RESINS



(57) Abstract: A curable composition comprising a) an epoxy resin having on average more than one epoxide group per molecule and b1) an alkyldipropylenetriamine of general formula (I) and/or b2) an adduct of an alkyldipropylenetriamine of general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule in which R is a hydrocarbon radical having 8 to 22 carbon atoms, and the

use of this composition for coating mineral and metallic substrates.

WO 01/21679 A1

**UTILITY DECLARATION
AND POWER OF ATTORNEY
Utility Application**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Alkyldipropylenetriamines and their adducts as hardeners for epoxy resins

the specification of which

- ☐ is attached hereto OR
☐ was filed on _____ as United States Application Serial No. ____ OR
☒ was filed on 14/09/00 as PCT International Application No. PCT/EP 00/08970
☐ and was amended on ____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Date of Filing (day/month/year)	Priority Claimed	
			Yes	No
199 45 643.7	Germany	23/09/99	<input checked="" type="checkbox"/>	<input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (day/month/year)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (day/month/year)	Status-Patented, Pending or Abandoned

POWER OF ATTORNEY: As a named inventor, I hereby appoint as my attorneys and/or agents, with full power of substitution and revocation, to prosecute this application and transact all business in the United States Patent and Trademark Office, and in countries other than the United States, and to do all things necessary or appropriate therefor before any competent International Authorities in connection with any international patent application(s) corresponding to the above-identified invention application, all of the registered practitioners identified by Customer Number 22249:



22249

PATENT TRADEMARK OFFICE

LYON & LYON LLP
Suite 4700
633 W. Fifth Street
Los Angeles, CA 90071
(213) 489-1600

Please direct all inquiries to Kristin H. Neuman, Esq. , at the above Customer Number. Ms. Neuman's direct line is (914) 681-8851 ext. 4603.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18, United States Code, § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

201	FULL NAME OF INVENTOR	FIRST Name Wolfgang	MIDDLE Initial _____	LAST Name SCHERZER	
	RESIDENCE & CITIZENSHIP	City Bergkamen	State or Foreign Country Germany	Country of Citizenship Germany	
	POST OFFICE ADDRESS	Schenkstrasse 10	City Bergkamen	State or Country Germany	Zip Code 59192

INVENTOR'S SIGNATURE W. Scherzer DATE 30/10/01

202

202	FULL NAME OF INVENTOR	FIRST Name Jörg	MIDDLE Initial _____	LAST Name VOLLE	
	RESIDENCE & CITIZENSHIP	City Selm/Bork	State or Foreign Country Germany	Country of Citizenship Germany	
	POST OFFICE ADDRESS	Luisenstrasse 37a	City Selm/Bork	State or Country Germany	Zip Code 59379

INVENTOR'S SIGNATURE Jörg Volle DATE 11.10.2001